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MAKING BORDEAUX MIXTURE AND SOME OTHER SPRAY- ING PROBLEMS

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MAKING BORDEAUX MIXTURE, AND SOME OTHER SPRAYING PROBLEMS

By W. S. FIELDS* and JOHN A. ELLIOTT.

Since the necessity of using Bordeaux sprays in the apple orchards in the Ozark region has been thoroughly demonstrated by experience, many inquiries have come to the Experiment Station as to the best methods of mixing the ingredients in making Bordeaux mixture, and also other questions of local importance in the making of sprays. This bulletin undertakes to answer the following questions: I. To determine the best methods and conditions for making Bordeaux mixture; II, To determine the effect of water hardness upon the suspension of ingredients in certain spray mixtures; III, To determine the amount of arsenic in solution in certain spray mixtures.

The chemical determination in all cases were made by Professor J. B. Rather of the department of Agricultural Chemistry of the Arkansas Experiment Station. The mixtures were made in amounts large enough to practically duplicate actual orchard conditions.

1. PREPARING BORDEAUX MIXTURE.

The work here presented on Bordeaux mixtures is largely a duplication of work done by Dr. O. Butler of New Hampshire Experiment Station, who has made fundamental investigations on the chemistry and on the physical properties of various copper sprays, (1, 2, 3, 4, 5.)

The Bordeaux mixture was prepared from stock solutions. The stock copper sulphate solution was made by dissolving copper sulphate in water at the rate of one pound to the gallon, and the stock milk of lime solution by mixing freshly slaked stone lime with water at the same rate. The different methods of mixing were as follows:

Method 1—Strong Lime Added to Weak Copper: 1.6 gallons of the stock milk of lime solution poured into 1.6 gallons of copper sulphate stock solution previously diluted by 16.8 gallons of water.

Method 2—Weak Lime Added to Strong Copper: 1.6 gallons of stock milk of lime solution diluted with 16.8 gallons of water poured into 1.6 gallons of stock copper sulphate solution.

*Most of this work was done by Mr. Fields before leaving Arkansas Experiment Station.

Method 3—Lime Added to Copper, Equal Strengths: 1.6 gallons of stock milk of lime solution diluted with 8.4 gallons of water, poured into 1.6 gallons of stock copper sulphate solution diluted with 8.4 gallons of water.

Method 4 (Check)—Lime and Copper, Equal Strengths, Poured Simultaneously Together: 1.6 gallons each of stock milk of lime and copper sulphate solutions diluted with 8.4 gallons of water.

Method 5—Copper to Lime, Equal Strengths: 1.6 gallons of stock copper sulphate solution diluted with 8.4 gallons of water, poured into 1.6 gallons of stock milk of lime solution diluted with 8.4 gallons of water.

Method 6—Weak Copper to Strong Lime: 1.6 gallons of stock copper sulphate solution diluted with 16.8 gallons of water, poured into 1.6 gallons of stock milk of lime solution.

Method 7—Strong Copper to Weak Lime: 1.6 gallons of stock copper sulphate solution poured into 1.6 gallons of stock lime solution previously diluted with 16.8 gallons of water.

Method 8—Hydrated Lime Bordeaux: This was made by the same method as No. 4 but using freshly hydrated lime instead of freshly slaked stone-lime.

The temperature of the water during the experiment was 20 degrees Centegrade, which is 68 degrees Fahrenheit.

TABLE I.

Effect of Method of Mixing Ingredients Upon the Settling in Bordeaux Mixture.

Method No.	Dilution	Amount of Sample	Temperature of Water Used	Settling at the End of 30 Min.	Settling at the End of 1 Hour	Settling at the End of 6 Hrs.	*Sphaerocrystals Counted Under microscope After 72 Hours.
1	4-4-50	20 Gal.	20 deg. C.	2.8%	13.4%	51.7%	35-Large crystals
2	"	"	"	46.4%	51.0%	88.0%	60-Small crystals
3	"	"	"	4.5%	32.0%	63.0%	80-Small crystals
4	"	"	"	3.1%	26.0%	66.0%	30-Large crystals
5	"	"	"	1.4%	3.1%	28.0%	25-Large crystals
6	"	"	"	1.4%	2.8%	20.0%	20-Large crystals
7	"	"	"	2.1%	24.3%	49.6%	100-Small crystals
8	"	"	"	1.7%	3.4%	40.2%	

*In counting the sphaerocrystals a Leitz microscope was used with a No. 8 Leitz compound ocular and a Leitz No. 4 mm. apochromatic objective.

For comparison with the sphaerocrystal count in Table 1, a sample of Bordeaux mixture made by each method was kept sealed each in a glass container. The examination was made of each mixture, 72 hours after mixing.

The quality of Bordeaux mixture is indicated by the length of time it remains in suspension and also by the presence of the so-called sphaerocrystals. The sphaerocrystals represent an insoluble and therefore inactive state of the product. When it reaches this state it is entirely worthless. The best product is the very slow settling gelatinous or colloidal precipitate obtained by pouring the dilute copper into the strong lime. From this stage the precipitate gradually becomes heavier and coarser until it forms the insoluble worthless crystals found in the old mixture. If this is reshaken, it settles again almost at once, like so much fine sand. The rate at which the original mixture settles is therefore an indication of how near the product is to the worthless crystalline state.

Of the eight methods tried, methods two and seven should be discarded because the product is not good as revealed both by settling, and by the number of sphaerocrystals present. Methods three, four, and five necessitate the use of large dilution tanks for one or both solutions and should be discarded in favor of methods one or six on this account.

The Bordeaux mixture made as in method six showed less precipitation and less sphaerocrystals than Bordeaux made by any of the other methods. This was the only mixture that would remain in suspension for any length of time upon being reshaken after once having settled. This proves the almost collidal nature of the precipitate formed by this method of mixing. The practical lack of sphaerocrystals indicates a relatively slow deterioration of this mixture as compared with the ordinary Bordeaux.

The simplest method of mixing this solution in field practice, has been found to put the required amount of water in the spray tank, add the stock bluestone solution, then start the engine. The stock lime solution is poured slowly through the screen while the weak copper solution is also pumped through the screen by the back flow from the pump. When all the lime has been added and thoroughly mixed, the lead arsenate is put in and the agitation continued a few minutes longer. This involves less work than any other method and has given the best results. **It eliminates the need for large dilution tanks for the two solutions, and makes the mixing of Bordeaux no more difficult than the mixing of lime sulphur solution. The thing to remember is that the copper sulphate should always be diluted before mixing, and never added in the concentrated solution either to a weak or a strong lime solution.**

The hydrated lime Bordeaux compared favorably with the mixture made from freshly slaked lime. In using fresh dry hydrated lime, **one third more** by weight of lime must be used for equal strength Bordeaux mixture made from stone lime. That is, if 4-4-50 Bordeaux is to be made, six pounds of **fresh** hydrated lime must be used where four pounds of stone lime would have been used. This is to make up for the water added in the process of hydration. If the lime is airslaked, that is, carbonated, it cannot be used for making Bordeaux mixture. For the same reason hydrated lime should be used only when it is known to be **fresh** and of high quality.

In the slaking of stone lime too great care cannot be taken in preventing drowning by applying too much water, or burning by allowing the lime to get too dry and hot during the slaking process. These are common faults.

Butler has shown (3) that there is greater difference in the deterioration of Bordeaux solution made at different temperatures than by different methods of mixing ingredients. At higher temperatures Bordeaux solution deteriorates very rapidly. The average temperature of spring and well water in the Ozark region is about 54 deg. Fahrenheit, an ideal temperature for making Bordeaux mixture. For this reason fresh well or spring water should be used in preference to pond water in making Bordeaux, and under any circumstances Bordeaux should be used immediately after mixing or else discarded.

II

EFFECT OF WATER HARDNESS UPON THE SUSPENSION OF INGREDIENTS OF SPRAY MIXTURES.

Method of Procedure:

Water samples of thirty gallons each, representing various degrees of hardness were collected in the vicinity of Fayetteville and some few artificially prepared in the laboratory as follows:

TABLE II.

Sample No	Source	Hardness	Hardness, Parts Per Million, Average of Three Trials
1	Tap water from White River	Soft	66.0
2	Distilled water from laboratory	Very soft	10.0
3	Artificial; distilled water, 55 gms. $MgSO_4$	Very hard	555.0
4	Artificial; distilled water, 60 gms. $CaCl_2$	Very hard	570.0
5	Artificial; tap water, clay one-half pound per gallon	Soft	61.0
6	Swaggerty Springs from Boone chert formation	Hard	157.0
7	Clear Creek	Hard	183.0

*American Public Health Assn; 1912, 2nd. Ed.-Lab. Sec.:00 32-34.

Water is classified as:

Soft, when it contains less than 100 parts of calcium or magnesium per million parts;

Hard, when it contains 300 to 500 parts of calcium or magnesium per million parts;

Very hard, when it contains more than 500 to 600 parts of calcium or magnesium per million parts.

Water hardness was determined by the titration of a known volume of the sample against a standard soap solution. The principle involved is that water of a given hardness has a certain soap destroying power. Therefore, the amount of soap destroyed by a given volume of water is an index of its hardness.

The soap and reagents were prepared in the laboratory. The reagents used were standardized by the station chemist and the soap solution standardized from these.

II-(A)-EFFECT OF WATER HARDNESS UPON THE SETTLING OF BORDEAUX MIXTURE.

The Bordeaux mixture was prepared from stock solutions of lime one pound per gallon, and copper sulphate, one pound per gallon. The temperature of the stock solutions when used was 20 degrees C. and the water varied from 18 degrees C. to 21 degrees C.

After addition of the lead arsenate paste at the rate of four pounds to one hundred gallons of water and thorough stirring, a liter sample was taken. To test the effect of water hardness upon the settling of ingredients, the Bordeaux mixture was made by the usual method. By this method, equal strengths of lime and copper sulphate were equally diluted and poured together simultaneously. The following table shows the results:

TABLE III.

Effect of Water Hardness Upon Precipitation of Ingredients in Bordeaux Lead-Arsenate

Amount 4-4-50 Mixture	Sample Number	*Lead Arsenate Grams Used		Settling in mm. After					
		Acid	Neutral	30 Minutes		2 Hours		24 Hours	
				A	N	A	N	A	N
20 Gal.	1 (soft)	181.5	181.5	58	31	141	122	161	160
"	2 (very soft)	181.5	181.5	8	48	37	124	145	146
"	3 (very hard)	181.5	181.5	4	2	20	26	120	143
"	4 (very hard)	181.5	181.5	8	47	33	124	142	160
"	5 (soft)	181.5	181.5	14	18	54	92	153	172
"	6 (hard)	181.5	181.5	3	3	22	24	134	159
"	7 (hard)	181.5	181.5	6	18	34	69	132	146

*The neutral lead arsenate used was manufactured by the Thomsen Chemical Company. It is known as "tri-plumbic" lead arsenate. The label on the package guarantees not less than 8.1% total metallic arsenic, equivalent to not less than 12.5% As_2O_3 (arsenic oxide) not to exceed 0.49% water soluble metallic arsenic, equivalent to 0.75% As_2O_3 and not to exceed 50% water. The acid lead arsenate was manufactured by Dow Chemical Company. It was guaranteed to contain not less than 15% arsenic oxide, less than $\frac{3}{4}$ of 1% soluble arsenic oxide.

The data of Table II do not show uniform results. This is to be expected owing to the various factors which might easily be involved. However, it appears that the hardest waters have a tendency to prevent rapid precipitation. Of the two types of hardness, the magnesium shows a less rapid precipitation than the calcium. The artificial water sample in which there was one half pound of clay per gallon represents an extreme type of muddy water. Because of the great amount of clay in mechanical suspension the rate of precipitation was rapid.

In general, the data show that the hardness of water has no great effect upon the rate of precipitation; that the more rapid precipitation occurs in solutions containing neutral arsenate of lead. For all practical purposes the kind of water used in preparing spray solutions, especially Bordeaux mixture, need not be given any attention, except that the extremely muddy type should not be used. Whether it is preferable to use acid or neutral lead arsenate does not enter this phase of the question.

II-(B)-EFFECT OF WATER HARDNESS UPON THE SETTLING IN LIME-SULPHUR SOLUTION.

The lime-sulphur solution was prepared at the station, using the Pennsylvania formula of 60-120-50. The ingredients were cooked with steam and the finished concentrated solution tested 27 degrees Beaume.

In each case five gallons of the water sample were used. This was made up to a strength of 4-100, using the concentrated lime-sulphur solution. This solution was divided into two equal parts of $2\frac{1}{2}$ gallons each. To one part, acid lead arsenate was added. After thoroughly stirring each solution containing the lead arsenate, a settling sample was taken and nearly all of the remainder used for an arsenate sample. The following table shows the results:

TABLE IV.

Effect of Water Hardness Upon Settling of Lime Sulphur-Lead Arsenate Solution.

Water Sample No.	Amount of Sediment in mm. After					
	30 Minutes		1 Hour		24 Hours	
	A	N	A	N	A	N
1	12	9	12	9	13	9
2	10	9	11	$9\frac{1}{2}$	14	$9\frac{1}{2}$
3	15	8	15	8	15	8
4*	16	10	16	10	16*	10*
5	121	163	179	184	193	196
6	15	7	15	8	18	9
7	18	9	18	9	18	11

*Lead arsenate caked on the cylinder bottom.

Table 111 shows little if any effect of water hardness upon sedimentation in lime-sulphur solution containing lead arsenate. There appeared to be a slight tendency toward less sedimentation with the softer waters except in the case of the artificial sample prepared with clay. The great amount of sediment occurring in the clay sample was to be expected.

Generally there was less sedimentation with the neutral lead arsenate than with the acid lead arsenate. In the lime-sulphur solution prepared with the calcium-hard water the lead arsenate in each case was found to be caked at the bottom of the cylinder.

III-AMOUNT OF ARSENIC IN SOLUTION IN CERTAIN SPRAY MIXTURES

By arsenic in solution is meant the amount of water soluble arsenic. The samples for water soluble arsenic determination were decanted from the different Bordeaux mixtures and lime-sulphur solutions after each had stood not less than two weeks. All of these determinations were made by the station chemist.

TABLE V.

A—Water Soluble Arsenic Oxide (As_2O_3) in Bordeaux-Lead Arsenate Mixtures.

Sample No.	Lbs. Lead Arsenate Per 100 Gallons	Water Hardness Parts per Gallon	As ₂ O ₃ Parts Per Million Official Method.*	
			Acid Arsenate	Neutral Arsenate
2269-1	4	183		1.9
2269-2	4	183		
2269-3	4	570	0.9	
2269-4	4	62	1.9	
2269-5	4	570		0.9
2269-6	4	10		2.8

*Official method for Bordeaux-Lead Arsenate mixture. Proable error .9 parts per million.

The above data indicates that the water soluble arsenic in the Bordeaux lead arsenate mixture was very small.

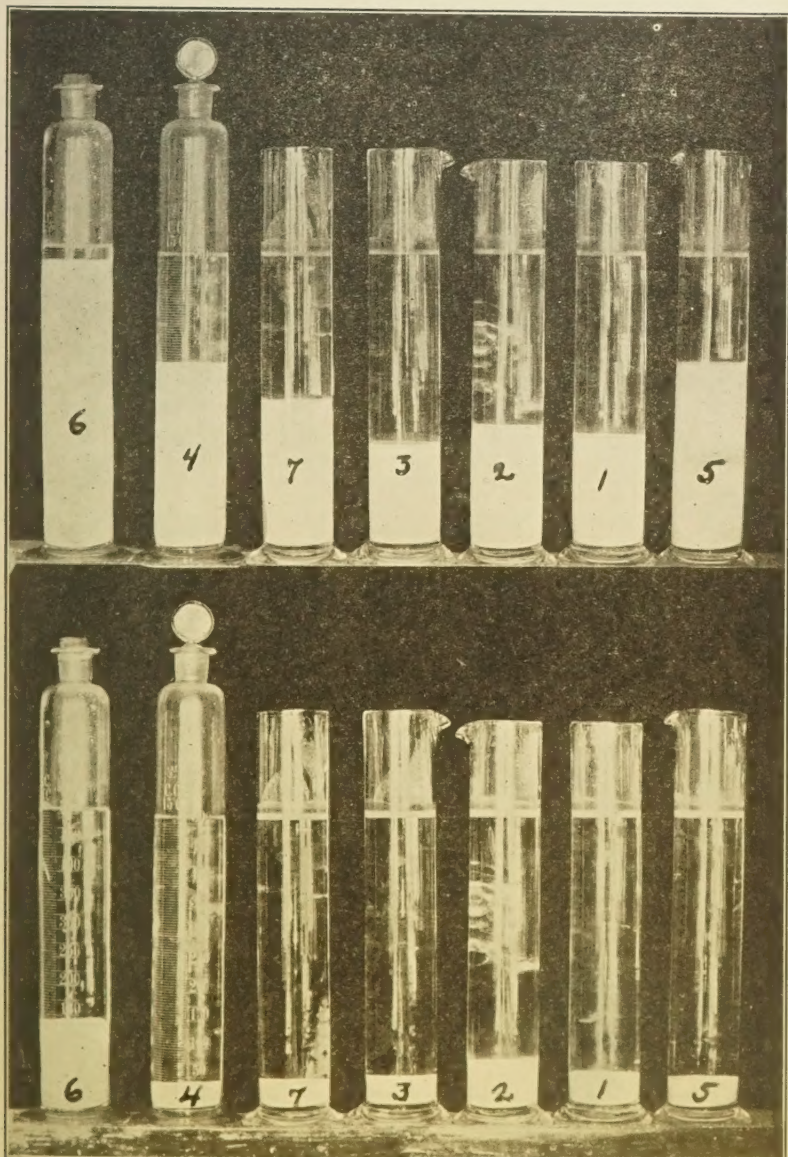
B—Water Soluble Arsenic in Lime-Sulphur-Lead Arsenate Solutions.

Sample No.	Lbs. Lead Arsenate Per 100 Gallons	Water Hardness Parts per Million	As ₂ O ₃ Parts Per Million			
			H ₂ SO ₄ Method		Na ₂ O ₂ Method	
			Acid	Neutral	Acid	Neutral
2283-1	8	61	1.7			
2283-2	8	183		1.7		11.2
2283-2	8	570		0.9		9.7
2283-4	8	570	3.5		14.3	
2283-5	8	10		5.1		14.3
2183-6	8	183	2.6		13.5	
2283-7	8	61		2.3		6.9
2283-8	8	555		0.8		5.8
2283-9	8	555	1.6		6.2	
2281-10	8	66		0.8		3.9
2283-11	8	10	1.6		5.4	
2283-12	8	66	1.6		4.6	
2283-13	8	157	2.3		10.0	
2283-14	8	157		0.8		6.2

As₂O₃ in precipitate (removed) formed on concentration: Na₂O₂ Method, none; H₂SO₄ Method, 0.0-0.3 mg. As₂O₃ in Na₂O₂, none. Probable error 0.8 parts per million.

Mr. Rather made the following explanation in submitting the results of analyses of lime-sulphur-lead arsenate solutions: "The method designated 'H₂SO₄' was the official method for Bordeaux-lead arsenate mixtures except that the precipitate caused by the acid was filtered off after coagulation. Analyses showed that the amount of arsenic lost by this process was within the limit of error.

PLATE I.



"The method designated as 'Na₂O₂' was as above except that the sulphur was decomposed with sodium peroxide. There was no arsenic found in the precipitate removed on acid coagulation. No arsenic was found in the sodium peroxide.

"I am unable to state which of these methods, if either, gives reliable results. As there was no arsenic in the peroxide and as there was no arsenic removed in appreciable amount from the solution as prepared by the H₂SO₄ Method, it would appear that the two methods should give concordant results."

In view of the above statement the analyses do not show conclusive results but may at least indicate that the water soluble arsenic in the lime-sulphur-lead arsenate solutions is small.

EXPLANATION OF PLATE

Relative Rapidity of Settling of Bordeaux Mixture Made By Different Methods of Mixing Ingredients. Upper Row: Settling After 1 hr.
Lower Row: Settling After 24 hrs.

CONCLUSIONS

1. The best method of mixing the ingredients in preparing Bordeaux mixture is that of pouring a very dilute solution of copper sulphate into a thick or strong lime solution as indicated in Method 6.

It is recommended that no old Bordeaux mixture be used for spraying trees or plants. This does not mean that old stock solutions of lime and copper sulphate cannot be utilized provided they are properly kept and not mixed until used.

2. Water hardness has no appreciable effect upon the precipitation of Bordeaux or Bordeaux-Lead Arsenate Mixtures; or sedimentation of Lime-Sulphur-Lead Arsenate solutions.

It is advisable to avoid very muddy waters for preparing spray mixtures.

3. The amount of arsenic in solution in Bordeaux or lime-sulphur spray mixtures when either acid or neutral lead arsenate is used is small.

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